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(71) Applicant: MITSUBISHI PETROCHEMICAL CO., LTD.
5-2, 2-chome, Marunouchi
Chiyoda-ku Tokyo100(JP)

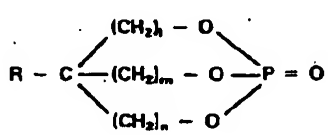
(72) Inventor: Tamura, Yutaka
4668, Ami Ami-machi
Inashiki-gun Ibaraki(JP)

(72) Inventor: Tanaka, Ryohei
405, Ogoso
Yokkaichi-shi Mie(JP)

(74) Representative: Diamond, Bryan Clive et al,
Gee & Co. Chancery House Chancery Lane
London WC2A 1QU(GB)

(54) Polyphenylene ether resin compositions.

(57) A composition comprises 100 wt. parts of a polyphenylene ether, optionally with other polymer substances, and 0.1 to 20 wt. parts of a bicyclophosphoric ester compound of formula:



where l = 0, 1 or 2, m and n = 1, 2 or 3, and R is hydrogen, C_1 - C_{19} alkyl or the group X–CH_2– where X is a carboxylic or phosphoric acid residue or an alkoxy group. 15 such ethers are named.

Optional other polymers include polymers of styrene, rubbers and thermoplastic polymers, including graft polymers. Fillers may be present.

The components can be blended in an extruder or plast mill.

The composition has improved flame-retardance without reduction of the inherent heat resistance of the polyphenylene ether.

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POLYPHENYLENE ETHER RESIN COMPOSITIONS

The present invention relates to a novel flame-retardant resin composition. More particularly, it relates to a flame-retardant resin composition which is superior in thermal properties and is composed of polyphenylene ether or a mixture thereof with another polymeric substance, and a bicyclophosphoric ester compound.

Polyphenylene ether as an engineering plastics is very useful because of its outstanding mechanical and thermal properties and self-extinguishing characteristics.

The flame-retardance of polyphenylene ether is not necessarily satisfactory. Moreover, polyphenylene ether has an extremely poor processability when used alone, and, in actual use, it is blended with styrene resin and other resins for the improvement of processability. (For blending with styrene resin, see U.S. Patent No. 3,383,435.) This blending impairs the self-extinguishing properties of polyphenylene ether and the blended polyphenylene ether is more combustible than the polyphenylene ether alone. Thus, ther is a demand f r improvement of the flame-r tardance of p lyphenylene ether.

In order to overcome the above-m ntioned drawback of

polyphenylene ether it is known to incorporate therein an aromatic phosphate compound such as triphenyl phosphate as a flame-retardant. Triphenyl phosphate imparts flame-retardance, but, at the same time, it lowers the heat distortion temperature because it also works as a plasticizer. Therefore, at present there are not satisfactory methods for making polyphenylene ether compositions flame-retardant.

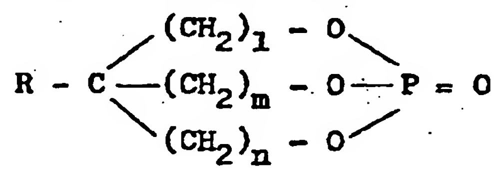
Accordingly, an object of this invention is to provide a satisfactory flame-retardant polyphenylene ether resin composition.

We have now found that polyphenylene ether can be made flame-retardant, without sacrificing the thermal properties, by adding a bicyclophosphoric ester compound.

The polyphenylene ether resin composition of this invention comprises:

(a) 100 parts by weight of a polyphenylene ether or a resin composition of polyphenylene ether and a polymeric substance, and

(b) 0.1 to 20 parts by weight of a bicyclophosphoric ester compound represented by the general formula:



wherein l is 0, 1 or 2, m and n each is an integer of 1, 2 or 3, and R is hydrogen or $C_1 - C_{19}$ alkyl or a derivative thereof.

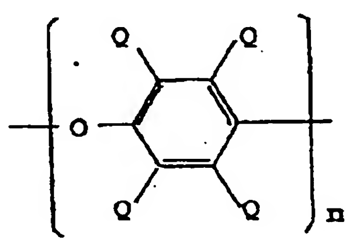
The polyphenylene ether resin composition of this invention has flame-retardance, and yet, unlike known compositions, the thermal properties of polyphenylene ether are impaired only a little by the addition of the flame-retardant.

In the accompanying drawings:-

Figures 1 and 2 are graphs showing the relationship between the heat distortion temperature and the average combustion time in the burning test according to the UL (Underwriters Laboratories, USA) Standards, Subject 94, of resin compositions obtained in some examples and comparative examples.

The polyphenylene ether used in this invention is disclosed in U.S. Patent Nos. 3,306,874, 3,306,875, 3,257,357, and 3,257,358, and other literature.

The preferred polyphenylene ether is a polymer having the repeating units represented by the formula:



wherein the oxygen atom in one unit connects to the benzene nucleus of the adjoining unit; n is a positive integer of 50 or over; and Q is a monovalent substituent selected from a hydrogen atom, halogen atom, hydrocarbon group having no tert-α-carbon atom, halogenated hydrocarbon group having at least two carbon atoms between the halogen atom and the phenyl nucleus, hydrocarbon oxy group, and halogenated hydrocarbon oxy group having at least two carbon atoms between the halogen atom and the phenyl nucleus.

Typical examples of polyphenylene ether include poly(2,6-dilauryl-1,4-phenylene) ether, poly(2,6-diphenyl-1,4-phenylene) ether, poly(2,6-dimethoxy-1,4-phenylene) ether, poly(2,6-diethoxy-1,4-phenylene) ether, poly(2-metho-

xy-6-ethoxy-1,4-phenylene) ether, poly(2-ethyl-6-stearyloxy-1,4-phenylene) ether, poly(2,6-dichloro-1,4-phenylene) ether, poly(2-methyl-6-phenyl-1,4-phenylene) ether, poly-(2,6-benzyl-1,4-phenylene) ether, poly(2-ethoxy-1,4-phenylene) ether, poly(2-chloro-1,4-phenylene) ether, and poly-(2,5-dibromo-1,4-phenylene) ether.

Examples of polyphenylene ether further include a copolymer of 2,6-dimethylphenol and 2,3,6-trimethylphenol, a copolymer of 2,6-dimethylphenol and 2,3,5,6-tetramethylphenol, and a copolymer of 2,6-diethylphenol and 2,3,6-trimethylphenol.

The polyphenylene ether used in this invention also includes modified polyphenylene ether in which the polyphenylene ether defined by the above-mentioned formula is grafted with a styrenic monomer such as styrene, _p_-methylstyrene and α-methylstyrene.

The examples of the polyphenylene ether corresponding to the above-mentioned formula are found in the specifications of the above-mentioned U.S. Patents.

The group of polyphenylene ethers preferred in this invention includes polyphenylene ether of the above-mentioned formula which has two alkyl substituents at the ortho positions with respect to the ether oxygen atom. In other words, each Q at the ortho position is alkyl, preferably $C_1 - C_4$ alkyl. Typical examples of this group include poly-

(2,6-dimethyl-1,4-phenylene) ether, poly(2,6-diethyl-1,4-phenylene) ether, poly(2-methyl-6-ethyl-1,4-phenylene) ether, poly(2-methyl-6-propyl-1,4-phenylene) ether, poly-(2,6-dipropyl-1,4-phenylene) ether, and poly(2-ethyl-6-propyl-1,4-phenylene) ether.

The most preferred polyphenylene ether resin in this invention is poly(2,6-dimethyl-1,4-phenylene) ether.

The polyphenylene ether composition may also contain other polymeric substances.

To improve moldability, the composition may contain a styrene resin. Examples of such styrene resin include a homopolymer of styrene such as polystyrene and poly-α-methylstyrene; high-impact polystyrene modified with butadiene rubber, styrene-butadiene copolym r, ethylene-propylene copolymer, or ethylene-propylene-diene terpolymer; and styrene-butadiene copolymer styrene-maleic anhydride copolymer, styrene-acrylonitrile copolymer, styrene-acrylonitrile-butadiene copolymer, and styrene-methyl methacrylate copolymer.

To improve impact resistance, the composition may contain a polymer substance such as natural rubber, polyisoprene, polybutadiene, styrene-butadiene copolymer, ethylene-propylene copolymer and ethylene-propylene-non-conjugated diene copolymer.

Moreover, the composition may contain

a thermoplastic resin such as polyethylene, ethylene-vinyl acetate copolymer, polypropylene, polyamide, polycarbonate, polyethylene terephthalate, and styrene-grafted polyolefin.

The composition may also contain

a reactive polymer produced by introducing polar groups into the above-mentioned elastomeric polymers or thermoplastic resins.

The reactive polymer can be produced by grafting the above-mentioned polymer with an unsaturated organic acid or an anhydride thereof (e.g., acrylic acid, methacrylic acid, maleic acid, itaconic acid, and anhydride thereof) or an unsaturated silane compound (e.g., vinyltrimethoxysilane, vinyltriethoxysilane, vinyltriacetoxysilane, γ-methacryloxypropyltrimethoxysilane, and propenyltrimethoxysilane), or by introducing metal ions into a part of the carboxyl group on the graft chain of the graft-modified polymer.

The reactive polymer can also be produced by block polymerization or random polymerization of ethylene with polar vinyl monomer (e.g., acrylic acid and ester thereof) or vinyl silane.

In the case where a reactive polymer is used, it is desirable to add an inorganic filler. When a reactive polymer and an inorganic filler are used in combination, the reactive polymer is dispersed in the matrix of polyphenylene

ether or a composition of polyphenylene ether and styrene resin, and the inorganic filler is selectively filled into the reactive polymer. This unique structure provides outstanding mechanical strength.

The inorganic filler includes titanium oxide, zinc oxide, talc, clay, calcium carbonate, and silica which are commonly used for synthetic resins.

The inorganic filler should preferably have an average particle diameter of 0.05 to 1.0 μm, and it should be added in an amount of 0.5 to 60 wt%, preferably 1 to 45 wt%, based on the resulting composition.

Other polymers that can be used include polyphenylene ether-grafted polyolefin or styrene resin-grafted polyolefin.

The polyphenylene ether-grafted polyolefin can be produced by grafting glycidylated polyphenylene ether, which is obtained by reacting polyphenylene ether with epichlorohydrin, onto a polyolefin having carboxyl group or acid anhydride on the main chain or side chain, such as ethylene-acrylic acid copolymer, ethylene-methacrylic acid copolymer, maleic anhydride-modified polypropylene, maleic anhydride-modified polyethylene, and maleic anhydride-modified ethylene-vinyl acetate copolymer.

The polyphenylene ether-grafted polyolefin can also be produced by grafting polyphenylene ether to a polyolefin

having a glycidyl group on the side chain such as ethylene-glycidyl methacrylate copolymer and ethylene-vinyl acetate-glycidyl methacrylate copolymer.

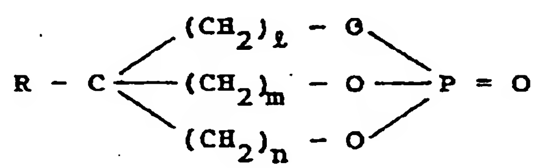
The polystyrene-grafted polyolefin can be produced by grafting a polyolefin having a glycidyl group on the side chain (e.g., ethylene-glycidyl methacrylate copolymer or ethylene-vinyl acetate-glycidyl methacrylate copolymer) to a styrene copolymer having a carboxyl group or cyclic acid anhydride on the main chain or side chain (e.g., styrene-maleic anhydride copolymer, styrene-citraconic acid anhydride copolymer, styrene-itaconic anhydride copolymer, styrene-asconit acid anhydride copolymer, styrene-acrylic acid copolymer, and styrene-methacrylic acid copolymer).

The grafted polyolefin can be added to the composition after graft polymerization; but in the case where a polyolefin containing a glycidyl group is used, the grafting reaction can be accomplished by mixing the polyolefin with polyphenylene ether or styrene resin having a carboxylic acid or anhydride group, at a high temperature of 150°C or more.

Mixing at a high temperature is preferred from the economical point of view, because the ingredients used are mixed uniformly and the polyphenylene ether-grafted polyolefin and/or polystyrene-grafted polyolefin can be produced all at once.

The above-mentioned polymeric substance should be added in an amount of 0 to 10,000 parts by weight, preferably 1 to 1,000 parts by weight, more preferably 25 to 400 parts by weight per 100 parts by weight of polyphenylene ether.

The bicyclophosphoric ester compound blended with the polyphenylene ether in this invention is represented by the general formula given above, namely:

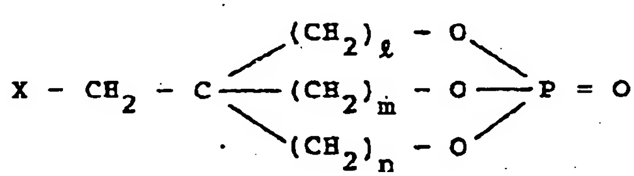


wherein *ℓ* is 0, 1 or 2, *m* and *n* each is an integer of 1 to 3, and R is hydrogen or $C_1 - C_{19}$ alkyl or a derivative thereof. This compound is described in, for example, "Organic Phosphorus Compounds", Vol. 6 (published by Wiley-Interscience, a Division of John Wiley & Sons, Inc.) and other publications.

Examples of bicyclophosphoric ester compounds include 2,6,7-trioxa-1-phosphobicyclo[2,2,2]octane-1-oxide, 2,6,7-trioxa-1-phosphobicyclo[2,2,2]octane-4-methyl-1-oxide, 2,6,7-trioxa-1-phosphobicyclo[2,2,2]octane-4-ethyl-1-oxide, 2,6,7-trioxa-1-phosphobicyclo[2,2,2]octane-4-hexyl-1-oxide, 2,6,7-trioxa-1-phosphobicyclo[2,2,2]octane-4-hexadecyl-1-

oxide, 2,6,7-trioxa-1-phosphobicyclo[2,2,2]octane-4-nitro-1-oxide, 2,6,7-trioxa-1-phosphobicyclo[2,2,2]octane-4-amino-1-oxide, 2,6,7-trioxa-1-phosphobicyclo[2,2,2]octane-4-hydroxymethyl-1-oxide, 2,8,9-trioxa-1-phosphobicyclo[2,2,2]nonane-5-methyl-1-oxide, and 2,6,7-trioxa-1-phosphobicyclo[2,2,2]heptane-4-methyl-1-oxide.

Examples of bicyclophosphoric ester compounds in which R is a derivative of an alkyl group include the compounds represented by the general formula:



wherein ℓ is an integer of 0 to 2, m and n each is an integer of 1 to 3, and X is a carboxylic acid residue, phosphoric acid residue, or alkoxy group.

Examples of such compounds include 2,6,7-trioxa-1-phosphobicyclo[2,2,2]octane-4-acetoxymethyl-1-oxide, 2,6,7-trioxa-1-phosphobicyclo[2,2,2]octane-4-benzoyloxymethyl-1-oxide, 2,6,7-trioxa-1-phosphobicyclo[2,2,2]octane-4-diphenoxyphosphinyloxymethyl-1-oxide, 2,6,7-trioxa-1-phosphobicyclo[2,2,2]octane-4-methoxymethyl-1-oxide, and 2,6,7-trioxa-1-phosphobicyclo[2,2,2]octane-4-ethoxymethyl-1-oxide.

The bicyclophosphoric ester compound is added in an

amount of 0.1 to 20 parts by weight, preferably 1 to 10 parts by weight, per 100 parts by weight of polyphenylene ether or a composition of polyphenylene ether and polymeric substance. If the amount added is less than 0.1 part by weight, the flame-retardance effect is not produced, and if it is more than 20 parts by weight, the physical properties of the resulting composition is adversely affected.

The flame-retardant polyphenylene ether resin composition of this invention can be produced by the blending method which is conventionally used for blending plasticizers, stabilizers, colorants, etc. with an extruder or plast-mill. In particular, the intended flame-retardant polyphenylene ether resin composition can be produced by extruding with a 25 mm extruder at a cylinder temperature of 240 to 330°C and a screw speed of 20 to 40 rpm, or by melt-mixing for 5 to 15 minutes with a plast-mill at a cell temperature of 240 to 330°C and a screw speed of 20 to 40 rpm.

The present invention will now be described in greater detail by reference to the following examples and comparative examples.

EXAMPLE 1

Production of composition:

A flame-retardant polyphenylene ether resin composition was prepared by mixing 50 parts by weight of poly(2,6-dimethyl-1,4-phenylene) ether having an intrin-

sic viscosity of 0.50 dℓ/g (measured in chloroform at 25°C), 50 parts by weight of high-impact polystyrene (475D, a product of Asahi Dow), and 5 parts by weight of 2,6,7-trioxa-1-phosphobicyclo[2,2,2]octane-4-ethyl-1-oxide. Mixing was accomplished for 10 minutes at 250°C using a plast-mill running at a screw speed of 40 rpm.

The flame retardance and heat distortion temperature of the resulting polyphenylene ether resin composition were measured according to the following methods. The results are shown in Table 1 and Fig. 1.

Burning test:

The flame retardance of the polyphenylene ether resin composition of this invention was evaluated according to the UL Standards, Subject 94.

A specimen, 15.25 cm long, 1.25 cm wide, and 1.6 mm thick, is suspended vertically by holding the top in a room where there is no air movement. The flame of a Bunsen burner so adjusted as to form a 1.9 cm long blue flame is applied to the lower end of the specimen. Ten seconds later, the burner is moved away. The duration of burning of the specimen is recorded (first combustion time).

Immediately after the flame on the specimen has gone out, the flame of a Bunsen burner is applied to the lower end of the specimen again for 10 seconds in the same manner as above. The duration of burning of the specimen is re-

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corded (second combustion time).

On the other hand, a piece of cotton is placed 30 cm under the specimen and whether or not the cotton catches fire when the burning resin drops is observed.

The above-mentioned tests are repeated for five specimens. The specimen is rated as 94VE-I if the maximum burning time is less than 30 seconds, the average burning time is less than 25 seconds, and all the specimens do not ignite the cotton. The specimen is rated as 94VE-II if at least one of the specimens ignites the cotton. The specimen is rated as 94VE-O if the maximum burning time is less than 10 seconds, the average burning time is less than 5 seconds, and all the specimens do not ignite the cotton. The specimen is rated as 94HB if the maximum burning time is more than 30 seconds or the average burning time is more than 25 seconds. The order of flame-retardance is 94VE-O, 94VE-I, 94VE-II, and 94HB.

Heat distortion temperature:

Measured as follows according to ASTM D-648.

A specimen, 126 mm long, 12.6 mm wide, and 6.3 mm thick, is heated at a rate of 2°C per minute under a flexural stress of 18.6 kg/cm^2. The temperature at which the deflection reaches 0.254 mm is the heat distortion temperature.

EXAMPLE 2

The same experiment as in Example 1 was carried out for a flame-retardant polyphenylene ether resin composition prepared in the mixing ratio as shown in Table 1. The results are shown in Table 1 and Fig. 1.

COMPARATIVE EXAMPLES 1 TO 3

The same experiment as in Example 1 was carried out for flame-retardant polyphenylene ether resin compositions in which triphenyl phosphate was used as a flame-retardant. The results are shown in Table 1 and Fig. 1.

COMPARATIVE EXAMPLE 4

The same experiment as in Example 1 was carried out for a polyphenylene ether resin compositions in which no flame-retardant was added. The results are shown in Table 1 and Fig. 1.

COMPARATIVE EXAMPLES 5 AND 6

The same experiment as in Example 1 was carried out for flame-retardant polyphenylene ether resin compositions prepared in the mixing ratio as shown in Table 1. The results are shown in Table 1 and Fig. 1.

Table 1

	Examples		Comparative Examples					
	1	2	1	2	3	4	5	6
C mponent of Resin Composition (parts by weight)								
Polyphenylene ether resin	50	50	50	50	50	50	50	50
High-impact polystyrene	50	50	50	50	50	50	50	50
Flame retardant								
Bicyclophosphoric ester compound	5	3	-	-	-	-	0.05	25
Triphenyl phosphate	-	-	7	5	3	-	-	-
Burning test (rating according to UL-94)	94VE-O	94VE-I	94VE-O	94VE-I	94VE-I	Burnt	Burnt	94VE-O
Heat distortion temperature (°C)	131	134	115	119	126	137	137	100

EXAMPLE 3

The same experiment as in Example 1 was carried out for a flame-retardant polyphenylene ether resin composition prepared in the mixing ratio as shown in Table 2, in which the high-impact polystyrene was replaced by acrylonitrile-butadiene-styrene copolymer (JSK-15, a product of Japan Synthetic Rubber Co., Ltd.). The results are shown in Table 2.

EXAMPLES 4 TO 9

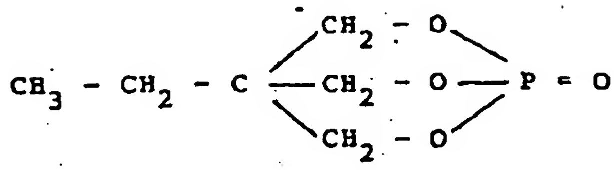
The same experiment as in Example 1 was carried out for flame-retardant polyphenylene ether resin compositions in which the 2,6,7-trioxa-1-phosphobicyclo[2,2,2]octane-4-ethyl-1-oxide was replaced by a variety of bicyclophosphoric ester compounds as shown in Table 2. The results are shown in Table 2.

Table 2

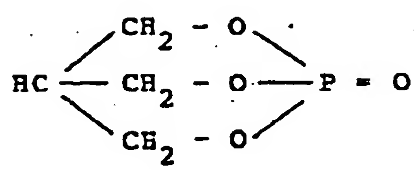
Components of resin composition (parts by weight)	Examples 3	4	5	6	7	8	9	Comparative Example 1
Polyphenylene ether resin	50	50	50	50	50	50	50	50
Polymeric substance								
High-impact polystyrene	-	50	50	50	50	50	50	50
ABS resin	50	-	-	-	-	-	-	-
Flame retardant								
Bicyclophosphoric ester compound	5 (A)	5 (B)	5 (C)	5 (D)	5 (E)	5 (F)	5 (G)	-
Triphenyl phosphate	-	-	-	-	-	-	-	7
Burning test (rating according to UL-94)	94VE-O	94VE-O	94VE-O	94VE-O	94VE-O	94VE-O	94VE-O	94VE-[illegible]
Heat distortion temperature (°C)	133	132	133	130	130	129	131	115

Structure of bicyclophosphoric ester compound

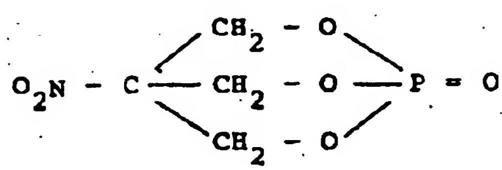
(A)



(B)



(C)



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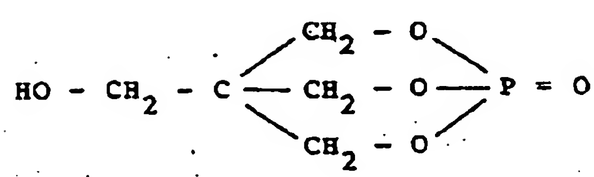

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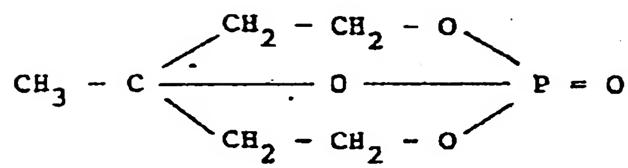

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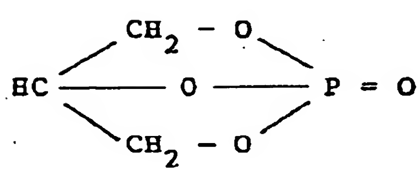
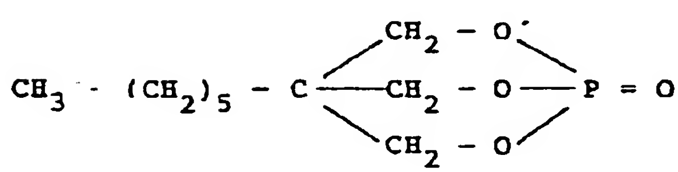


(G)



EXAMPLE 10

The same experiment as in Example 1 was carried out for a flame-retardant polyphenylene ether resin composition in which 5 parts by weight of 2,6,7-trioxa-1-phosphobicyclo[2,2,2]octane-4-benzoyloxymethyl-1-oxide was used. The results are shown in Table 3 and Fig. 2.

EXAMPLE 11

The same experiment as in Example 10 was carried out for a flame-retardant polyphenylene ether resin composition prepared in the mixing ratio as shown in Table 3. The results are shown in Table 3 and Fig. 2.

COMPARATIVE EXAMPLES 7 TO 9

The same experiments as in Example 10 were carried out for flame-retardant polyphenylene ether resin compositions prepared in the mixing ratio as shown in Table 3, in which triphenyl phosphate was used as the flame-retardant. The results are shown in Table 3 and Fig. 2.

COMPARATIVE EXAMPLE 10

The same experiment as in Example 1 was carried out for a flame-retardant polyphenylene ether resin composition in which no flame-retardant was added. The results are shown in Table 3 and Fig. 2.

COMPARATIVE EXAMPLES 11 AND 12

The same experiments as in Example 10 were carried out for flame-retardant polyphenylene ether resin compositions prepared in the mixing ratio as shown in Table 3. The results are shown in Table 3 and Fig. 2.

EXAMPLE 12

The same experiment as in Example 10 was carried out for a flame-retardant polyphenylene ether resin composition prepared in the mixing ratio as shown in Table 4, in which the high-impact polystyrene was replaced by acrylonitrile-

butadiene-styrene copolymer (JSK-15, a product of Japan Synthetic Rubber Co., Ltd.). The results are shown in Table 4.

EXAMPLES 13 TO 15

The same experiments as in Example 10 were carried out for flame-retardant polyphenylene ether resin compositions in which the 2,6,7-trioxa-1-phosphobicyclo[2,2,2] octane-4-benzoyloxymethyl-1-oxide was replaced by a variety of bicyclophosphoric ester compounds as shown in Table 4. The results are shown in Table 4.

Table 3

	Examples		Comparative Example					
	10	11	7	8	9	10	11	12
Component of Resin Composition (parts by weight)								
Polyphenylene ether resin	50	50	50	50	50	50	50	50
High-impact polystyrene	50	50	50	50	50	50	50	50
Flame retardant								
Bicyclophosphoric ester compound	5	10	-	-	-	-	0.05	25
Triphenyl phosphate	-	-	7	5	3	-	-	-
Burning test (rating according to UL-94)	94VE-I	94VE-I	94VE-O	94VE-I	94VE-I	Burnt	Burnt	94VE-O
Heat distortion temperature (°C)	133	135	115	119	126	137	137	110

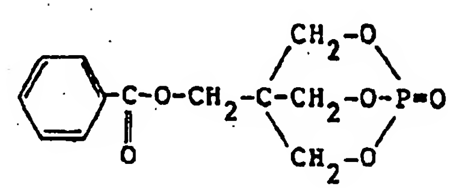
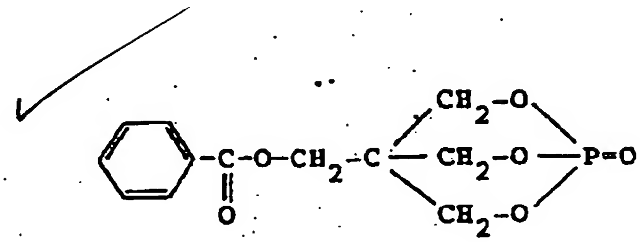
Structure of bicyclophosphoric ester compound: (H) 

Table 4

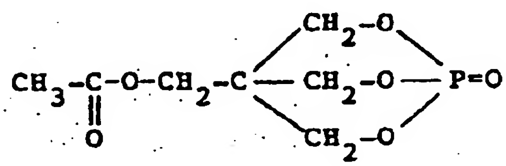
	Examples				Comparative Example 8
	12	13	14	15	
Components of resin composition (parts by weight)					
Polyphenylene ether resin	50	50	50	50	50
Polymeric substance					
High-impact polystyrene	-	50	50	50	50
ABS resin	50	-	-	-	-
Flame retardant					
Bicyclophosphoric ester compound	5 (H)	5 (I)	5 (J)	5 (K)	-
Triphenyl phosphate	-	-	-	-	5
Burning test (rating according to UL-94)	94VE-I	94VE-I	94VE-I	94VE-I	94VE-I
Heat distortion temperature (°C)	134	133	134	135	119

Structure of bicyclophosphoric ester compound:

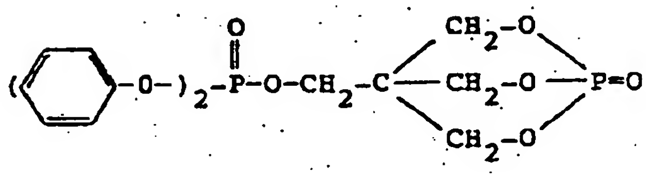
(H)



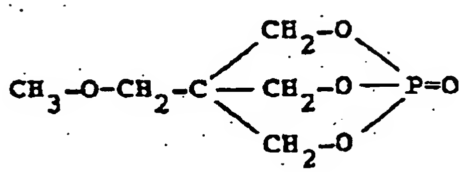
(I)



(J)



(K)



EXAMPLES 16 AND 17

Polyphenylene ether resin compositions were prepared by mixing the following components in the ratio as shown in Table 5 using a super-mixer and then the resulting compositions were melted at 280°C and pelletized using a twin-screw extruder (PCM-45ϕ, made by Ikegai Iron Works, Ltd.).

Poly(2,6-dimethyl-1,4-phenylene)ether (made by Mitsubishi Petrochemical Co., Ltd., having an intrinsic viscosity of 0.47 as measured in chloroform at 30°C);

Polystyrene (HF-77, a product of Mitsubishi Monsanto) Maleic anhydride-grafted ethylene-propylene copolymer (a product of Mitsubishi Petrochemical Co., Ltd., containing 1.5 wt% of maleic anhydride);

Styrene-butadiene copolymer (1502, a product of Japan Synthetic Rubber Co., Ltd.);

Precipitated calcium carbonate (having an average particle diameter of 0.5 μm); and

2,6,7-trioxa-1-phosphobicyclo[2,2,2]octane-4-hexyl-1-oxide.

The pellets were molded into prescribed test pieces using an injection molding machine, Model N-100, made by The Japan Steel Works, Ltd. The test pieces were subjected to burning test according to the UL standards, and the heat distortion temperature of the test pieces was measured. The results are shown in Table 5.

COMPARATIVE EXAMPLES 13 AND 14

Examples 16 and 17 were repeated except that the 2,6,7-trioxa-1-phosphobicyclo[2,2,2]octane-4-hexyl-1-oxide was replaced by triphenyl phosphate. The results are shown in Table 5.

Table 5

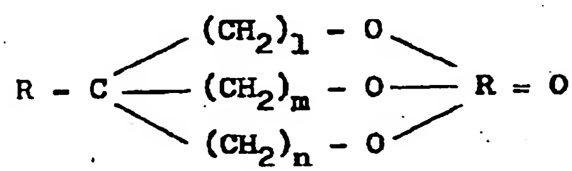
	Example 16	Example 17	Comparative Example 13	Comparative Example 14
Formulation (parts by weight)				
Poly(2,6-dimethyl-1,4-phenylene) ether	45	45	45	45
Polystyrene	45	45	45	45
Maleic anhydride-grafted ethylenepropylene copolymer	5	5	5	5
Styrene-butadiene copolymer	5	5	5	5
Calcium carbonate	5	5	5	5
2,6,7-trioxa-1-phosphobicyclo[2,2,2]octane-4-hexyl-1-oxide	5	3	-	-
Triphenyl phosphate	-	-	8	5
Measurements				
Heat distortion temperature (°C)	112	115	93	98
Burning test (UL-94)	94VE-O	94VE-I	94VE-I	94HB

Claims:

1. A polyphenylene ether resin composition comprising

100 parts by weight of polyphenylene ether resin or a resin composition comprising polyphenylene ether and other polymer substances, and

0.1 to 20 parts by weight of a bicyclophosphoric ester compound represented by the general formula



wherein **l** is 0, 1 or 2, **m** and **n** each is an integer of 1, 2 or 3, and R represents a hydrogen atom or an alkyl group having 1 to 19 carbon atoms or a derivative thereof.

2. A polyphenylene ether resin composition as claimed in Claim 1, wherein the resin composition comprises 100 parts by weight of polyphenylene ether and 1 to 1000 parts by weight of polystyrene or other polymeric substances.

3. A polyphenylene ether resin composition as claimed in Claim 1, wherein the resin composition comprises 100 parts by weight of polyphenylene ether and 1 to 1000 parts by weight of rubber-modified polystyrene.

4. A polyphenylene ether resin composition as claimed in Claim 1, wherein the resin composition comprises 100 parts by weight of polyphenylene ther and 1 to 1000 parts by weight of polystyrene, polyphenylen ther-graft d poly-olefin r polystyrene-grafted polyol fin.

5. A polyphenylene ether resin composition as claimed in Claim 1, wherein the resin composition comprises 100 parts by weight of polystyrene and reactive polymer, said reactive polymer being dispersed in the matrix of polyphenylene ether and polystyrene and an inorganic substance being further dispersed in said dispersed phase.

6. A polyphenylene ether resin composition as claimed in Claim 1, wherein in the bicyclophosphoric ester R is $X\text{-}CH_2\text{-}$ wherein X is a carboxylic acid residue, phosphoric acid residue or alkoxy group.

D. C. DIXON, B.Sc., C.P.A.
A. J. A. SUBB, C.P.A.
B. C. DIAMOND, M.Sc., C.P.A.
A. J. MOORE, M.A. (Oxon.), B.Sc., C.P.A.

Office Manager:
D. F. BROWN

Gee & Co.

CHARTERED PATENT AGENTS
TRADE MARK & DESIGN AGENTS
EUROPEAN PATENT ATTORNEYS

CHANCERY HOUSE,
CHANCERY LANE,
LONDON WC2A 1QU

Guildford Office & Accounts:
39 Epsom Road,
Guildford, Surrey, GU1 3LA
Telephone: Guildford 577007

Our Ref: 4/MS Your Ref: 30th November, 1983.

European Patent Office.
Receiving Section,
P.B. 5818 Patentlaan 2,
2280 HV RIJSWIJK (ZH),
The Netherlands.

Dear Sirs,

European Patent Application No. 83306468.6
Mitsubishi Petrochemical Co., Ltd.

We find clerical errors at pages 29 and 31 where one "R" in the general formula should be "P", as at page 10.

We enclose new pages 29 and 31 to correct these errors.

Yours faithfully,

B C Diamond

The request for correction is allowed under R. 88 EPC.
THE HAGUE 05 JAN. 1984
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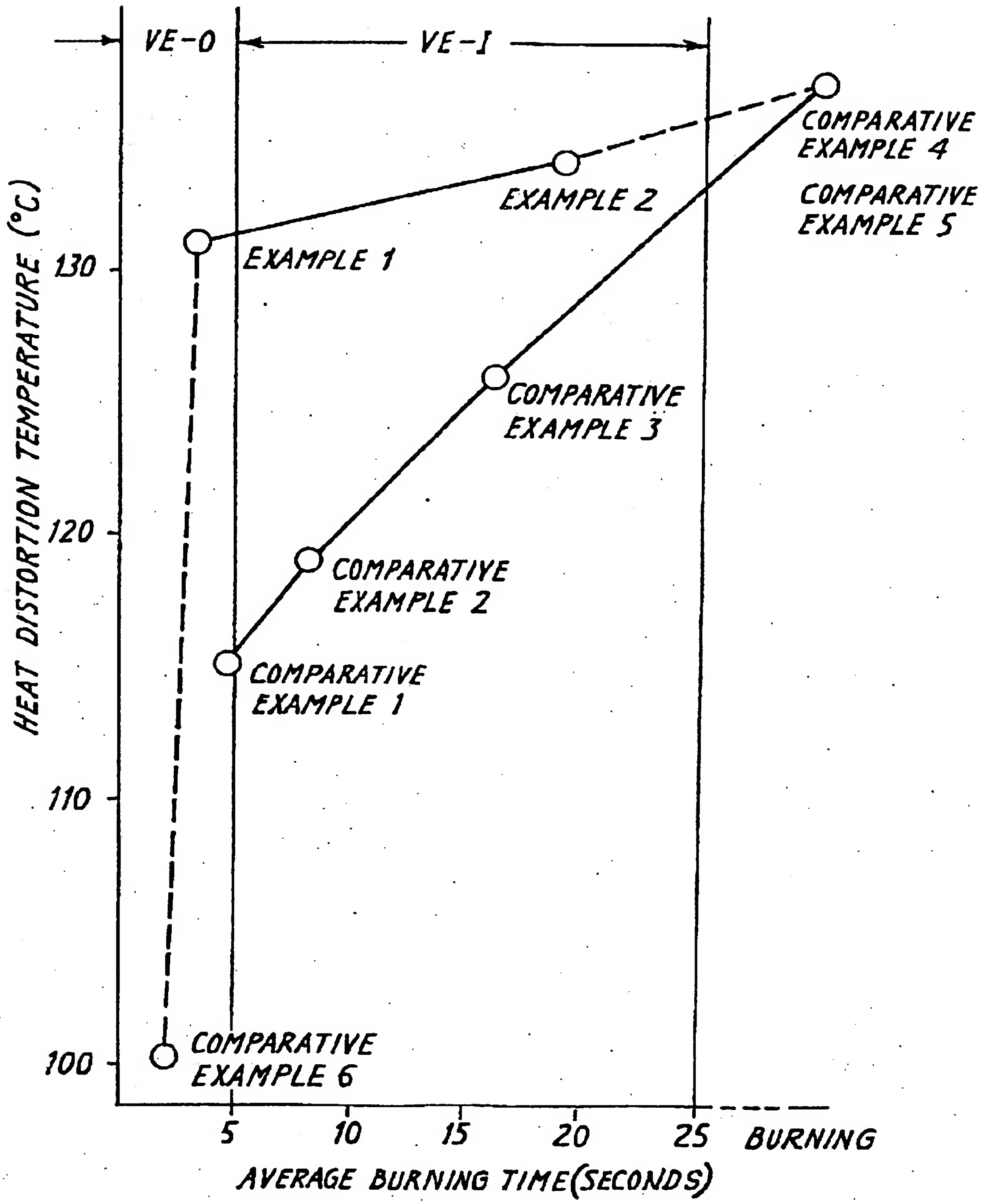
VE-0
VE-I
HEAT DISTORTION TEMPERATURE (°C)
130
120
110
100
EXAMPLE 1
EXAMPLE 2
COMPARATIVE EXAMPLE 4
COMPARATIVE EXAMPLE 5
COMPARATIVE EXAMPLE 3
COMPARATIYE EXAMPLE 2
COMPARATIVE EXAMPLE 1
COMPARATIVE EXAMPLE 6
5
10
15
20
25
BURNING
AVERAGE BURNING TIME(SECONDS)

FIG.1

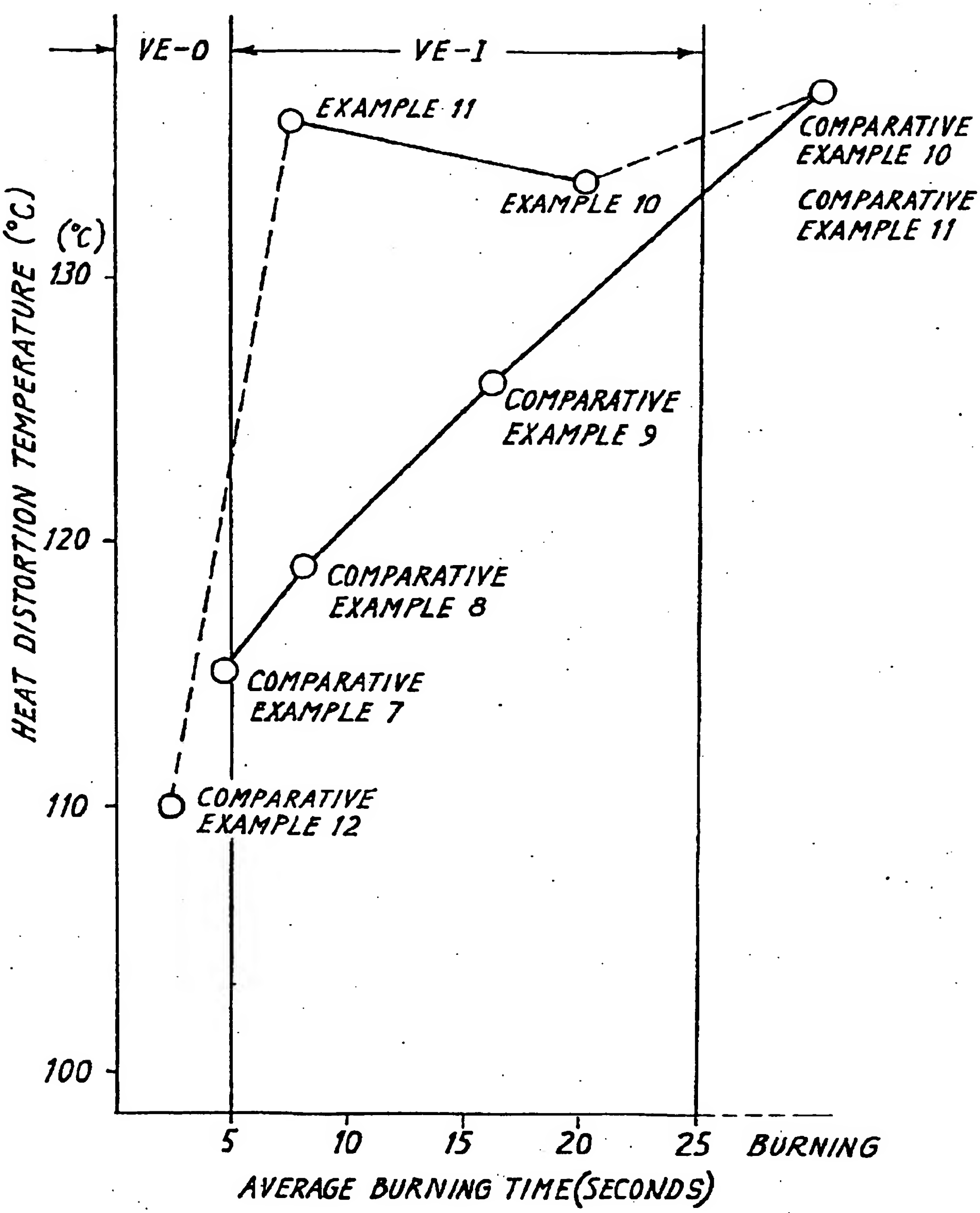
VE-0
VE-I
EXAMPLE 11
EXAMPLE 10
COMPARATIVE EXAMPLE 10
COMPARATIVE EXAMPLE 11
COMPARATIVE EXAMPLE 9
COMPARATIVE EXAMPLE 8
COMPARATIVE EXAMPLE 7
COMPARATIVE EXAMPLE 12
HEAT DISTORTION TEMPERATURE (°C)
(°C)
130
120
110
100
5
10
15
20
25
BURNING
AVERAGE BURNING TIME(SECONDS)

FIG.2

European Patent Office

EUROPEAN SEARCH REPORT

0116200
Application number

EP 83 30 6468

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
X	CH-A- 552 629 (CIBA-GEIGY AG) * Claim; example 6; column 4, line 19 *	1-6	C 08 K 5/52 C 08 L 71/04 C 08 L 25/04 C 08 L 51/06 C 08 L 55/02
Y	US-A-3 189 633 (W. CHANG et al.) * Claims 1,2; column 7, lines 27-30 *	1-6	
Y	US-A-3 293 327 (I. HECHENBLEIKNER et al.) * Claim 20; column 2, lines 23-34 *	1-6	
A,D	US-A-3 383 435 (E. CIZEK) * Claims *	2-4	

TECHNICAL FIELDS SEARCHED (Int. Cl. 3)

C 08 K
C 08 L

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	07-05-1984	HOFFMANN K.W.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

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